GENTNER – a miniaturised LIBS/Raman instrument
for the comprehensive *in-situ* analysis of the Martian surface

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ABSTRACT

We introduce a novel instrument to determine in-situ rapidly and with relatively high sensitivity (down to 10 ppm) the concentrations of many elements in Martian rock, coarse fine and soil samples with a lateral resolution of <1 mm. At the same time the instrument will provide information on possible organic components as well as mineralogical information. Detection of the life-related elements like H, C, N, O, P, S and Fe and investigation of their 3D-distributions as well as their occurrences in the various Martian materials may be indicative of biological activity.

The proposed instrument is a combination of Laser Induced Breakdown Spectroscopy (LIBS) and Raman Spectroscopy and meets the requirements concerning advanced in-situ analytical tools, like short measurement duration, high sensitivity, high repetition rate, high reproducibility, low mass, size and resource needs and high flexibility with respect to type, shape and size of sample material.

1. INTRODUCTION

The European Space Agency (ESA) recently started a program of exploration of Mars with the ultimate goal to have a manned mission to the planet within the year 2050. However, before getting to this ambitious and challenging task, a thorough exploration of the planet is needed both for scientific purposes and for the identification of hazards and local resources for the human exploration activities by detecting ions or radicals adsorbed on the environment and characterise the geochemical composition of the rocks. In the first phase, a major task will be to look for evidences of the existence of life, either extinct or extant.

There are two major avenues to hunt for potential past or present life on Mars. One is to directly search for evidence of biological activity such as organic matter or bio-mineralisations. Alternatively and complementarily, the study of the exogenic dynamics stored in the Martian sedimentary record will provide constraints on conditions, under which past or present life may have existed. The investigation of the sedimentary archive is based on the detailed characterisation of the chemical and mineralogical constitution of primary materials and its weathering products. Furthermore, it is essential to determine the chemical and mineralogical fractionation trends that occurred during disintegration and weathering of primary materials, during sediment transport and deposition since the nature of the chemical fractionations and mineralogical transformations will provide insight into the respective processes degrading the primary material and forming the sediments which in turn mirror the surface environmental conditions on ancient Mars. Thus the main goal will be to identify chemical trends or mineral phases that are diagnostic for specific processes and environments. Weathering under warm and wet conditions would have produced typical secondary mineralogical remnants such as clay minerals; hydrothermal activity and acid fog weathering would produce sulphates and chlorides; biological activity could be the source of carbonates and iron oxides such as magnetite.

The analysis should not be limited to the surface: because active plate tectonics probably ended many millions of years ago, the Martian sedimentary record represents the long-term exogenic cycle. A subsurface characterisation will allow to derive information on the evolution of surface conditions during the geologic past by applying sedimentological principles to soil profiles. In particular, the variation of element concentrations with depth will allow to reconstruct past changes in the contributions from different source materials. Given that the evolution of the meteoritic infall rate with time is known, a Ni-concentration depth profile in Martian regolith may provide insight into the evolution in the rate of soil formation during the geologic past. In addition, the depth distribution of the elements S, Cl,

Br, Li, Zn and Ba may reveal the effects of volcanic aerosols and hydrothermal activity.

To efficiently carry out these studies, several instruments are needed to perform a complete molecular and elemental analysis (see the study of the Exobiology Team of the ESA for a complete review [1]). The instruments proposed include Mössbauer spectrometers [2,3], chromatographic instrumentation [4,5], alpha proton X-ray spectrometers [6], Raman spectrometers [7, 8], mass spectrometers [9], X-ray diffractometers [10], electromagnetic subsounding devices [11] and a drill to analyse samples not oxidised by the intense UV radiation reaching the planet's surface.

For the molecular analysis a Raman spectrometer presents a number of advantages because of his high

Fig. 1. Raman spectrum of meteorite ALH8401(white matrix) showing silicates and carbonates peaks.
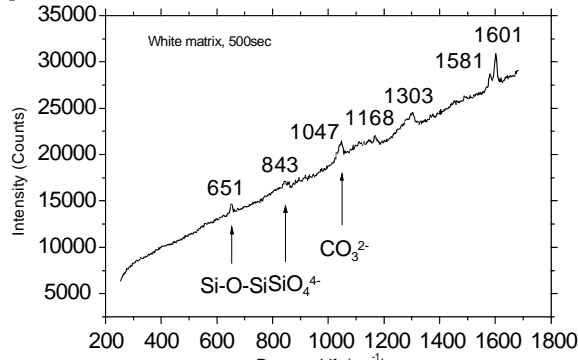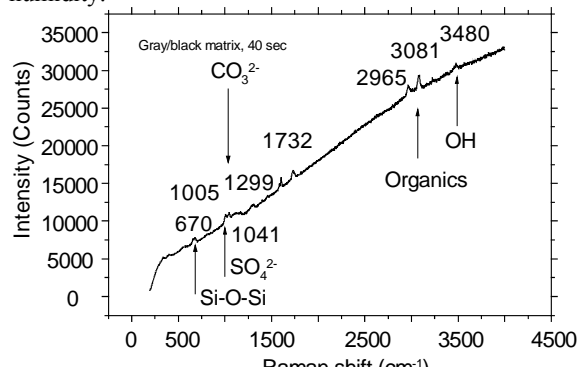

Fig. 2. Raman spectrum of meteorite ALH8401 (grey/black matrix) showing silicates, carbonates and sulphates peaks as well as the presence of organic contamination and humidity.


spatial resolution, sensitivity, relatively short integration time and non destructiveness which allow to analyse the same sample also with other techniques. It has, however, some drawbacks. First of all, the excitation laser beam may excite a fluorescence emission of the sample which, being usually several orders of

magnitude stronger than the the Raman signal, can hide the information. Another disadvantage is paradoxically the extreme sensitivity of the technique. Raman scattering is heavily influenced by both the molecular composition and the geometrical arrangement of the sample[12]: even when the chemical composition is the same, the position of the lines varies depending on the molecular geometry. Furthermore, the position of Raman lines is also influenced by the phase of the sample and by its reological properties. To study unambiguously and completely a sample, its elemental content should therefore be independently known.

A solution to this problem can be found by using Laser-Induced Breakdown Spectroscopy (LIBS) which can quickly provide a full elemental analysis of the sample. Furthermore, LIBS and Raman can share a large number of subsystems thus allowing the saving of resources in the payload.

Fig. 3. LIBS spectrum of Andesite under Martian conditions.
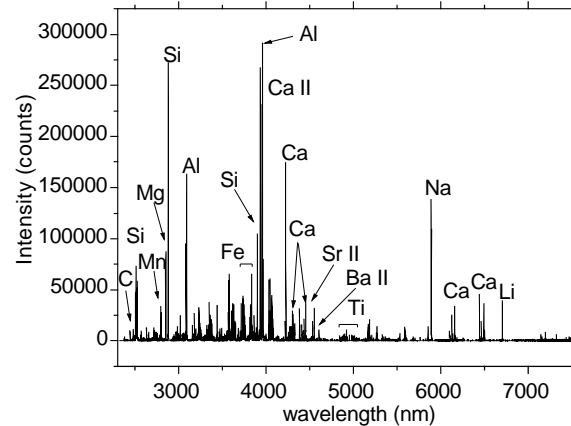
A combined Raman/LIBS spectrometer can therefore perform an important role in the context of planetary exploration –see Fig. 1 – 3 for examples of the potentialities – for its advantages:

1. No sample preparation needed;

2. Fast *in-situ* determination of the element concentrations down to 100 ppm and with a lateral resolution above 100 μm of all kinds of samples encountered *via* LIBS;

3. Elemental analysis immune from interferences from dust layers;

4. Elemental depth profiling;

5. Raman spectroscopy provides information on the mineral composition;

6. Raman spectroscopy provides information on the presence and molecular composition of organic components;

7. Raman spectroscopy can be used as probe technique for reactions of chemicals with Martian materials on microchips.

The possibility of such an integration has been thoroughly analysed in a theoretical exercise called LIRAMIS [13]. A prosecution of that study is ongoing [14]and will lead to a fully functional breadboard by the end of 2006. The innovative instrument, named GENTNER after the physicist and cosmochemist Wolfgang Gentner (1906 – 1980), greatly profits from synergistic effects, sharing the optical spectrometer, the lasers, and on-board data reduction facilities [15].

2. SPECIFIC GENTNER SCIENCE

The complementary nature of the chemical and structural information that GENTNER will return from a single spot on the target material renders unequivocal phase identification, which will be greatly enhanced by linking the sets of complementary data through the application of mineralogical concepts. Pristine, cosmic material, which is continuously delivered to the Martian surface through meteoritic infall, contains considerable quantities of organic matter – the prerequisites for the evolution of life. Organic material has, however, not yet been detected on the surface of any planet. The absence of organics on the Martian surface despite of this continuous meteoritic delivery is ascribed to the reactivity of the Martian soil. This reactivity that possibly involves adsorbed super-oxide is obviously a result of an intense atmosphere-surface interaction under strong solar UV radiation. It has important implications for future human space-flight and for Exobiology in general. Super-oxide species, however, are not yet identified on Mars. The GENTNER instrument can identify, at least qualitatively, such radicals. High quality mineralogical characterisation is a prerequisite for the identification of surface adsorbed molecular or ionic species by means of Raman spectroscopy. Radicals not only drive the degradation of organic matter, they also contribute to oxidative weathering of primary minerals. From earlier missions we know that in the Martian regolith iron and sulphur occur in their highest oxidation states. Provided, that this is not the case in the magmatic and meteoritic precursor materials, the Martian surface acts as an oxygen sink and in this respect has a considerable effect on the composition of the Martian atmosphere. Although GENTNER will not be able to directly distinguish between oxidised and reduced iron and sulphur it provides the basis for normative calculations to identify the minerals, which host these species.

Given the present day ambient and subsurface environment, precipitates such as water ice, solid CO_2 and gas hydrates such as clathrates may be stable on Mars. The Raman spectroscopy part of GENTNER is a powerful tool to identify and characterise such species. Cryo-volcanism – instead of liquid water – may have played an dominant role in the formation of the channel features on the Martian surface. Vertical profiling of ices and clathrates could help to unravel this intensely debated uncertainty.

Table 1 summarises the possible applications of GENTNER in the different disciplines inherent the planetary exploration.

Discipline	Measurement	Science
Exobiology	Signatures of organic species	Analysis of molecular structures; Analysis of biofilm; Presence of present or past life
Organic chemistry	Reaction of materials with specific reagents	Presence and analysis of organic matter
Atmospheric Science	Adsorbed neutrals, ions and radicals	Interaction of Martian weather with solids
Mineralogy	Bio-mineralisations	Identification of mineral phases; Grain size distribution; Viscosity; Mechanical processes
Geochemistry	Bulk chemical composition	Abundances of major, minor and trace elements; Depth profiling; Geologic and geochemical history; Discrimination between surface species and bulk rock and minerals

Table 1. Range of applications of GENTNER instrument.

3. GENTNER CONCEPT

In the view of the deployment of the GENTNER instrument in an actual lander several experimental scenarios are foreseeable:

1. The instrument should analyse the material extracted from the drill in real time and outside the lander to take decisions on the opportunity to continue or stop the excavation phase;

2. The device should help to preselect which samples to be passed to subsequent and time-intensive instruments such as mass spectrometers or chromatographs inside the lander [16].

It is clear that the design should be kept flexible and modular to be able to accomodate these different needs. The basic design idea was to separate the main part of the instrument or Instrument Module (IM) and the needed optics for delivery/collection of the light or Sensor Head (SH), the two main subsystem being connected by fibre optic links. The IM contains the main subsystems composing the device: the excitation lasers, the spectrometer whilst the SH contains all the optics needed to shape the excitation beams, to collect the emitted radiation and to provide a visual image of the sample to ease the interpretation of the results.

This concept also allows to connect more than one head to the IM allowing to measure in more than one location with the same instrument (*e.g.* inside and outside a lander).

4. INSTRUMENT MODULE

4.1. Excitation lasers

Two different laser sources are needed owing to the different wavelengths and regimes of operation. For both Raman and LIBS measurements, a careful analysis of the scientific requirements is needed to select the proper source.

The efficiency of Raman scattering is inversely proportional to the the fourth power of excitation wavelength. Although a blue-green laser may appears the best choice, this is not the case because such a laser will also excite a considerable fluorescence in the sample.

Excitation wavelength (nm)	Raman spectral range shift 200 – 3100 cm-1 (nm)	Normalised Raman efficiency
532	538 – 637	100
633	641 – 848	50
660	669 – 830	42
670	679 – 846	40
705	715 – 902	32
720	731 – 927	30
750	761 – 977	25

Table 2.Spectral ranges corresponding to a shift 200 - 3100 cm^{-1} and scattering efficiency for some wavelengths.

Furthermore, one has to consider that the most useful Raman signal will be shifted towards longer wavelengths with respect to the laser line. The maximum shift allowable depends on the molecules that are investigated. For the scientific requirements of the mission one can assume a maximum shift of 3100cm^{-1} which covers all major geological and biological features. This imply that the laser line should be selected so that the maximum shift will be detectable with a Silicon detector to be able to use the same detector for both Raman and the LIBS measurements. Table 2 shows the Raman spectral ranges corresponding to shifts 200 – 3100cm^{-1} as well as the corresponding scattering efficiencies for a selection of laser lines. It is quite evident that a laser source that simultaneously satisfy all the requirements should have emission in the range 600-720 nm.

The selected laser should be ideally monochromatic and free of mode hopping since Raman measurement are done relatively to the laser frequency. Since a reasonable bandwidth for the expected samples is about 8 cm^{-1} (~0.5nm in the spectral range of interest), the wavelength should be stabilised within ±0.2nm .

A laser emitting in this range can be either a wavelength-stabilised laser diodes or diode pumped solid state lasers (DPSSL). In the latter case a frequency-doubled Nd:YAG laser exploiting the line at 1348 nm will be used. Both lasers can be used with a proper design of the sensor head. The power required to collect Raman spectra in a reasonable time is about 5 mW.

Also in case of LIBS trade-offs have to be considered. The LIBS signal in given experimental conditions mainly depends on the sample ablation rate which is in turn determined by the sample physical and chemical properties such as optical absorption, thermal coefficients, grain size, surface roughness , matrix composition. Given the variety of the geological materials that could be found on Mars, and their different physical characteristics – *e. g*. dust, naturally or artificially compacted material, rocks, soil mixtures with CO_2 ice, etc. very different ablation rates and consequently LIBS signals are to be expected.

Although also for LIBS short wavelengths look attractive, a Q-switched Nd:YAG laser operating at standard λ=1064 nm should be used since the advantages to use shorter wavelengths will be offset by the increase of the system complexity (weight, volume) and of the sensibility on misalignment. Furthermore, the laser should be focused with a spot size in the range 50 – 500 μm to increase the ablation rates that can be obtained by a given laser pulse energy.

The laser energy should then be selected so that the energy density is above the ablation threshold for all the types of samples that are expected on Mars surface or subsurface (drilling cores), thus allowing for LIBS determination of at least principal constituents and major elements. Although different recent publications

report LIBS measurements in simulated Martian environment, they were performed by using very different experimental configurations and spectrometers/detection systems, and were considering mainly the soil samples, which are easier to ablate than the compact rocks such as basaltic rocks. So, the straightforward comparison between the results of different authors is not possible.

In the case of basaltic rock – the most difficult sample expected – the ablation of the sample and the LIBS emission has been reported [17] with an energy density of $1.05 J/cm^2$ over 10ns pulses. For soil samples, the LIBS signal increases and more elements can be detected by applying the same laser energy. The ablation rates in simulated Martian conditions are reported in table 3.

Material	Ablation rate per shot (μm)
Weathered basaltic layer	0.6 – 1.2
Dust (sand)	0.1 – 0.25

Table 3: Ablation rates per shot in simulated Martian conditions as reported in ref. [17].

Knight [17] also reported the limits of detection for the major constituents of expected samples as shown in table 4.

Element	Ba	Cr	Cu	Li	Ni	Pb	Sn	Sr
LOD (ppm)	21	39	43	20	224	95	84	1.9

Table 4: Limits of detection for the main constituents of the Martian rocks as reported in ref. [17].

Other elements, elements such as C, N, and O represent a special case. Their LOD is expected to be above 1% due to interference of the surrounding atmosphere on LIBS signal. Also for S, a LOD above 1% might be expected [18]

In conclusion for LIBS in Martian conditions a Nd:YAG laser emitting 4mJ and pulse length of 5 ns is sufficient to ablate the Martian rocks when focused in a spot smaller than 250µm.

The current baseline for GENTNER sources is summarised in table 5.

	LIBS	Raman
Operation mode	Pulsed	Continuous wave
Wavelength	1064 nm	600 – 700 nm
Wavelength stability	Uncritical	< 0.2nm
Sample irradiance	>500 MW/cm^2	<1KW/cm^2
Spot size	50 – 100 µm	20 – 50 µm

Table 5. Main characteristics of the laser sources needed for GENTNER.

4.2. Spectrometer system

Giving the required technical inputs in terms of spectral range and resolution, the expected intensities of the lines to be detected and the need to have a one-shot measurement as LIBS destroys the first layer of the samples more than one spectrometer design can be devised. In any case, if the full spectral range needed for LIBS and Raman (200 – 1000nm) is to be measured with a spectral resolution of 0.1nm which is required to resolve the plasma lines, there is no alternative to the use of high diffraction orders which will give superimposed spectra. To separate the orders there are two approaches: the first foresees a multiple order spectrometer concept with a single entrance slit. This spectrometer uses one grating to cover the full spectral range by measuring either the 1st, 2nd or 3rd spectral order. The proper order is selected by an optical filter array placed immediately behind the entrance slit and driven by a piezoelectric motor. In this spectrometer design, short wavelength spectra are analysed by higher diffraction orders (*e.g.* 2nd and 3rd), whereas long wavelength spectra are analysed by the fundamental order. Obviously also several laser shots are required to cover the entire spectra range for a LIBS measurement. This spectrometer has been extensively used in the LIRAMIS project [15].

Parameter	Raman	LIBS
Echelle grating	RGL 413 E 27 grooves/mm, 70° blaze angle	RGL 407 E 46.1 grooves/mm, 32° blaze angle
Order	20	92
Slit size	200x200µm	40x40µm
f/#	f/10	f/10
Specral resolution per 3 pixels	25pm@200nm, 125pm@1000nm	0.20nm@720nm, 0.25nm@900nm
Detector	EMCCD DV885 1002x1004	EMCCD DV885 1002x1004

Table 6. Key specification of the twin Echelle spectrometer.

The most interesting design foresees the use of an Echelle spectrometer. An Echelle grating is coarse, but is used at very high diffraction orders (typically 10 – 100). In comparison to the other spectrometer configuration, this design simultaneously produces spectra of many diffraction orders that are superimposed to each other at the focal plane. The separation between the different orders is obtained by using another diffraction element dispersing the light in the normal direction respect to the first one. Such element can be another grating, a prism or a combination of the two (grism). The problem of this configuration lays in the

different requirements for the optimisation of the UV and IR portion of the spectra. The solution is to use a twin spectrometer in a so-call "butterfly" configuration. In this configuration, two slits are used for the short and the long range so that both ranges are separately optimised. The preliminary design of this spectrometer allowed to draw the specifications listed in table 6.

5. SENSOR HEAD

For the design of the SH the starting point is the choice of the geometrical scheme of illumination detection. Considerations of mechanical stability towards variations of temperature and of ease of alignment, prompt for a coaxial arrangement in which the light of the two lasers is combined in a single beam. This configuration offers several advantages:

- Identical spots are measured with both analysis;

- The spot on the sample does not move if the distance changes slightly as in LIBS depth profiling;

- Distance control can be achieved by a simple mechanical stop. The mechanical stop can be also used as a shield against environmental light (for example, a conical tube around the measurement beam);

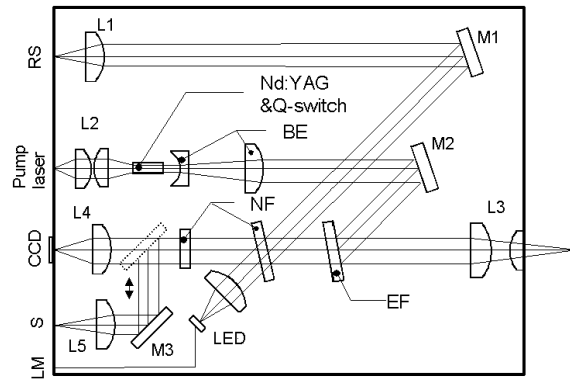- No opto-mechanical elements for focusing are

Fig. 4. Block scheme of the sensor head with Bragg grating filtered laser diode as source for Raman. RS Raman excitation from the instrument module; Pump Laser emission from the pumping laser diode; Nd:YAG &Q-switch laser active medium and passive Q-switch crystal; M1, M2, M3 mirrors; L1 collimator, L2 coupling optics, L3 front optics for focusing/collection; L4, L5 focusing optics, BE beam expander, EF dichroic edge filter, NF notch filters, LED laser monitor. M3 is movable to switch between the visual inspection and the spectral operational modus.

needed.

The current baseline for the design of the SH is shown in Fig. 4 and foresees a Bragg grating wavelength-stabilised laser diode and a Q-switched Nd:YAG laser as sources for Raman and LIBS measurements, respectively. The design keeps into account the possibility of integration with a microscope and/or close up imager that will share its objective lens with the beam delivery subsystem.

The wavelength-stabilised Raman source is placed inside the cavity as well as the pumping diode for the Nd:YAG laser where the environment temperature is less severe and they are connected by fibre optic links to the sensor head. The laser cavity of the Nd:YAG laser is however placed inside the sensor head to reduce the problems of coupling high peak power densities into the optic fibres. Special solarisation-resistant tapered optic fibres will be used to further reduce the power density on the fibre surface and to decrease the sensitivity to lateral misalignments. These fibres can be gold-plated to withstand the severe Martian conditions.

For what concerns the Raman branch, the light is first collimated and the beam is deflected by a folding mirror onto a notch filter. This filter reflects the light in an extremely narrow band around the laser line and is highly transmissive for all the other wavelengths. After passing through a high-pass edge filter, which has the function to combine the two laser beams, the light is finally focused onto the sample. On the other side of the notch filter an LED is foreseen as laser power monitor. Its output will be used to normalise the detected Raman signals removing any influence of the excitation power fluctuations.

For the LIBS branch, the pumping light will be coupled in the active medium in a standard stable laser cavity with intracavity passive Q-switching crystal. The infrared laser emission will be shaped by the beam expander BE which has the double role of reducing the power density on the dichroic edge filter EF and to reduce the spot size on the sample since the spot size is given by

$$w = \frac{2f}{D} \tag{1}$$

where w is the spot size, f is the focal length of the lens and D is the diameter of the area of the lens illuminated by the laser beam. The laser beam is then coupled in the front optics L3 whose focal length will be of the order of few centimetres to prevent the deposition of Martian matter on the lens surface during the LIBS measurements.

When starting from the sample, the emitted radiation is collected by the same optics used for the focusing. With this configuration, the coincidence between the

illuminated spot and the detection area is ensured even if for some reason a slight misalignment should occur the only consequence being a decrease of the intensity. After crossing the edge filter, the radiation is filtered by a couple of notch filters which provide an attenuation of the Raman line of the order of 10^{-8}. A movable mirror allows the selection between a spectral channel where an optical fibre is used to connect the measurement head to the spectrometer and an inspection channel where a proper focusing optics is used to form an image on CCD sensor. This inspection channel can be designed either to work as close up imager. The illumination of the sample will be carried out by using LEDs.

It should be pointed out that to the best of our knowledge, no space testing has been carried out on the Bragg grating wavelength-stabilised laser diode. Therefore, other alternative designs have been taken into account in the case that the suggested laser diode could not be used in the space environment. The backup solution has been identified in using a frequency-doubled Nd:YVO$_4$ laser operating at $\lambda= 664$nm. the Raman branch will be conceptually identical to the LIBS one with the pumping laser diode in the IM and a laser cavity and beam expander in the SH. However, giving the tight tolerances in the alignment of the Nd:YVO$_4$ and of the frequency doubling crystals a stable alignment is not easy to realise. Therefore, this approach shows some risks and additional work on the laser design is to be foreseen.

6. BUDGETS

Finally the budgets of GENTNER for what concerns the mass, power consumption, thermal power dissipated and

Subunit	Mass (g)
Instrument Module	
Laser drive unit	172
Pump laser	295
Raman laser system	41
Spectrometer	333
Spectrometer detector	59
Proximity electronics	141
Housing	157
External interconnections	47
Subtotal	*1245*
Sensor Head	
LIBS/Raman system	215
Imager	94
Subtotal	*309*
Total	**1554**

Table 7. Foreseen mass budget of GENTNER.

data generation are shown in tables 7– 10. For completeness also the data pertinent to the optional colour imager are reported.

Measurement	Peak Power (W)	Energy(Wh)
LIBS spectrum acquisition	6.8	0.057
Raman spectrum acquisition	7.2	0.060
Data transfer	4.3	
Idle mode	2.5	N/A
Colour image acquisition	3.2	0.054

Table 8. Power absorption of GENTNER

Measurement	Instrument Module (W)	Sensor Head (W)
LIBS spectrum acquisition	5.3	1.5
Raman spectrum acquisition	7.0	0.2
Data transfer	4.1	0.1
Idle mode	2.4	0.1
Colour image acquisition	2.5	0.7

Table 9.Thermal power dissipated during GENTNER operation.

Measurement	Data, uncompressed	Data compressed (libgzip)
LIBS spectrum	158 kByte	70kByte
Raman spectrum	52.5kByte	21kByte
Colour image	4.096MByte	450kByte
Housekeeping	200Byte	N/A

Table 10 Data budget of GENTNER.

7. CONCLUSIONS

GENTNER is in advanced stage of development and a fully functional breadboard is expected to be ready at the end of 2006. The breadboard will be available to all scientists of the team to develop proper databases prior the deployment of the device in the Martian environment.

8. ACKNOWLEDGEMENTS

This paper is the result of the efforts of a large team of 26 scientists and engineers from 6 different European countries and from academic and industrial environments. Although the complete list is too long to be reported in this paper, their contribution has been invaluable to draft the scientific needs for GENTNER.

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